SPECTROCHEMICAL INVESTIGATION OF THE
BALA AND STOCKDALE INTRUSIONS,
RILEY COUNTY, KANSAS

by

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INTRODUCTION

General Geologic Setting

Five ultramafic intrusions cut Permian sedimentary rocks in Riley County, Kansas. Two of these, the Bala and Stockdale intrusions, were studied during this investigation and are located as follows:

Bala, a low hill near the northeast corner of $NW\frac{1}{4}$ $NW\frac{1}{4}$ Sec. 6 T9S R5E.

Stockdale, in a stream bed on the north line of $NW\frac{1}{4}$ $SE\frac{1}{4}$ Sec. 23 T8S R6E.

Numerous inclusions of sedimentary, igneous, and metamorphic rocks imbedded in a fine-grained groundmass give these intrusions a brecciated appearance.

Previous Work

Moore and Haynes (1920) have discussed the petrography of the Bala intrusion in some detail (see Table 1.). Bridge (1953) reported on the petrography and the inclusions of these intrusions. Chemical studies include a whole rock analysis of the Stockdale intrusion by Sperry (1929) and analysis of red garnet from the Stockdale intrusion by Bagrowski (1941) (see Table 2.). Magnetic surveys of the area have been done by Dreyer (1947), Cook (1955), Baysinger (1963), and Dowell (1964). General discussions of these intrusions have been presented by Jewett (1941), Taylor (1950), and Byrne, Parish, and Crumpton (1956).

Method of Investigation

This study is an investigation of the Bala and Stockdale intrusions by emission spectrography. Magnetite and serpentinized olivine from the Bala intrusion and magnetite, phlogopite, garnet, chromite and serpentinized olivine* from the Stockdale intrusion were selected for analyses because

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*Serpentinized olivine is referred to as serpentine throughout the remainder of this paper.

Table 1.   Minerals of the Bala Intrusion.
(Moore and Haynes, 1920)

Sample 1.		Original Mineral
Mineral Present		
Serpentine	75%	Olivine
Calcite	15%	Augite
Chlorite		Biotite
Chromite		Chromite
Apatite		Apatite

Sample 2.

Serpentine	60%	Olivine
Calcite	30%	Augite
Chlorite		
Chromite		Chromite
Brucite		
Magnetite		Magnetite

(1) they were readily separated and (2) represent phases of primary and secondary origin. Titanium, zirconium, chromium, copper, cobalt, and nickel were chosen for study. The geochemical characteristics of these elements are such that they may provide data relative to petrogenetic theories.

Careful petrographic control permitted the data to be evaluated with respect to paragenetic relationships. X-ray diffraction analysis of two types of garnet found in the Stockdale intrusion supplemented the study.

An attempt was also made to use spectrochemical methods to determine the concentrations of rubidium and strontium in the samples studied because concentration data aids in chemical studies preliminary to Rb-Sr age determination.

PETROGRAPHY AND PETROLOGY

Hand Specimen Description

The most outstanding feature of the hand specimen from the Stockdale

Table 2a.   Chemical analysis* of the Stockdale Intrusion.
(Sperry, 1929)

SiO_2	24.15
Al_2O_3	2.03
Fe_2O_3	6.51
FeO	1.85
MgO	24.45
CaO	15.87
K_2O	.30
H_2O+	8.50
H_2O-	.85
TiO_2	1.50
CO_2	12.04
P_2O_5	.62
SO_3	.20
	98.87

Table 2b.   Chemical analysis* of red garnet from the
Stockdale Intrusion.   (Bagrowski, 1941)

SiO_2	40.42
Al_2O_3	21.12
Cr_2O_3	7.90
Fe_2O_3	10.50
MgO	14.42
CaO	4.71
	99.07

* method of analysis is unknown

intrusion is the highly brecciated appearance produced by numerous inclusions of sedimentary, igneous and metamorphic origin. These inclusions are imbedded in a dark green, fine-grained groundmass. Phenocrysts of garnet, phlogopite, and chromite give the rock a porphyritic texture. Magnetite and secondary calcite are also readily identified in the sample. The highly fractured nature of the Stockdale intrusion is exemplified by numerous random veins of calcite.

Since the inclusions and random veins of calcite are not as numerous in the Bala intrusion as in the Stockdale intrusion, hand specimens tend to be a dense, dark green rock. The rock has a porphyritic texture with phenocrysts of chromite. Magnetite and secondary calcite are also recognized in hand specimens. The Bala and Stockdale intrusions can be classified a serpentinized ultramafic rock.

<div align="center">Thin Section Description</div>

The Bala and Stockdale intrusions are petrographically quite similar. The most noticeable feature is the abundance of olivine and pyroxene pseudomorphs. These minerals have been replaced by antigorite, calcite, and magnetite. Pseudomorphs of olivine are the most common which suggests that the original rock was a peridotite or kimberlite.

The minerals present and their general mode of occurrence is shown in table 3. All of the minerals with the exception of chromite, garnet, Stockdale phlogopite, and some magnetite are secondary minerals. Large subhedral corroded grains, some almost entirely altered to chlorite, and undulatory extinction exhibited by these grains indicate primary crystallization of the Stockdale phlogopite. The paragenetic relationship of magnetite is not certain, but its euhedral to subhedral shape indicates that it crystallized

Table 3.   Occurrence and approximate percent of minerals.

Mineral	Occurrence	Estimated Percentage Bala	Stk*
Antigorite	alteration product of olivine and pyroxene, disseminated throughout the groundmass.	58	50
Calcite	Alteration product of olivine and pyroxene, disseminated throughout the groundmass and in veins.	17	20
Chlorite	alteration product of olivine, pyroxene and phlogopite in Stockdale, disseminated throughout the groundmass.	7	4
Magnetite	disseminated throughout groundmass, alteration product of olivine and pyroxene in psuedomorphs.	14	10
Ilmenite	disseminated throughout groundmass.	1	trace
Leucoxene	alternation product of ilmenite.	trace	trace
Hematite	alteration product of magnetite	trace	2
Phlogopite	primary mineral in subhedral grains.	trace	3
Biotite	alteration product of olivine and pyroxene.	trace	trace
Chrysotile	alteration product in veins.	trace	1
Zircon	disseminated throughout groundmass.	trace	trace
Garnet	primary mineral in anhedral grains.		4
Chromite	primary mineral in anhedral grains.	trace	4
Talc	disseminated alteration product.		trace
Silica	chert and quartz in inclusions.		trace

* Stockdale

before most of the groundmass. Undoubtedly there is primary and secondary magnetite in both intrusions. The fine-grained euhedral magnetite is predominant.

Petrology

Petrographic evidence indicates that the original olivine-pyroxene rich magma could be classified as near-ultramafic in composition. Serpentinization subsequently destroyed olivine and pyroxene either during injection in an aqueous environment or by the action of ground water after emplacement. Since the inclusions are well preserved, it is thought the temperature during injection was moderately low. Bowen and Tuttle (1949) suggest that injection of a peridotitic magma in an aqueous environment could occur at temperatures as low as 400°C. Such low temperature injections indicate that intrusion occurred in a plastic "mush" state rather than as a true magma. The water in the environment not only aided in the serpentinization but also lubricated the mass as it moved (Sosman, 1938). The source of the water may be from the original magma or from the intruded sediments.

Serpentinization during injection of the near-ultramafic magma in an aqueous environment agrees with petrographic evidence. As stated previously, the secondary magnetite probably crystallized early in the stages of serpentinization under near-magmatic conditions. Garnet, chromite, phlogopite and probably some magnetite were the only primary minerals that escaped complete serpentinization.

The last step in the sequence of events was fracturing of the rock and emplacement of calcite veins. This probably occurred during a post-emplacement period of tectonic activity resulting from contraction during cooling and secondary deposition of calcite by ground water. In the light of existing evidence, the rock may be classified as a serpentinized peridotite (P. S.

Wingard, personal communication).

ANALYTICAL PROCEDURE

Sample Preparation

Preliminary Preparation. Fresh samples from the Bala intrusion were obtained from the field with the help of Dr. Wingard. Since the Stockdale intrusion is exposed in a stream bed where fresh samples were not readily acquired, fresh core samples were obtained from the Geology Department. These samples were broken with a rock trimmer that had been thoroughly cleaned. Cleaning was accomplished by removing excess grease and dirt with a cloth than scrubbing the trimmer with water. To further guard against contamination, paper was spread around the base of the trimmer. The samples were then crushed with a carbide steel mortar and pestle which had been scrubbed with soap and water and rinsed with demineralized water and acetone. The Bala sample and the Stockdale sample were treated similarly.

The Stockdale sample was not crushed further at this point. Since it contained large grains of phlogopite, garnet, and chromite, hand picking with tweezers and the aid of a binocular microscope was sufficient for mineral separation.

The Bala sample was crushed, then sieved, using 100 mesh and 200 mesh sieves, by shaking in a Rotap machine. The sieves were cleaned in the same manner as the steel mortar and pestle. After the sieving was completed, the +200 -100 mesh fraction was ready for mineral separation.

Mineral Separation. After the sample from Bala had been crushed and sieved, the +200 -100 mesh fraction was divided into a light mineral fraction

and a heavy mineral fraction by use of heavy liquids. Bromoform and Tetrabromoethane were both used with equal success. A small amount of sample was added to a separatory funnel containing the heavy liquid. This mixture was stirred and permitted to settle. The heavy mineral fraction was drawn off into a beaker placed beneath the funnel. This was repeated until the entire sample was processed. The two fractions were washed with acetone several times to remove the heavy liquids and allowed to dry. It was found that Bromoform-separated grains were more easily cleaned than those separated with Tetrabromoethane. A typical separation left calcite, quartz, and chert in the light fraction, whereas, magnetite, chromite, and serpentine were concentrated in the heavy fraction. The magnetite-serpentine fraction was washed several times with acetone to remove any calcite that adhered to the grains. The magnetite was separated from the serpentine by use of a small hand magnet wrapped in weighing paper. This proved to be a very good method for extracting not only magnetite, but also for removing high magnetic impurities from other samples.

Desired purity of the magnetite fraction was achieved by repeated crushing in a small agate mortar and pestle and use of the hand magnet. Fine grains of non-magnetic material produced during crushing were removed by washing the magnetite sample in demineralized water and acetone and decanting the fine material. Stockdale magnetite was separated in the same manner. The purity achieved in the mineral separations is shown in table 4.

Initial separations of garnet, chromite, and phlogopite from the Stockdale sample were done by hand picking as described earlier. The phlogopite fraction was purified further by slight crushing and repeated hand picking until desired purity was achieved. The phlogopite fraction was then briefly rinsed in .5N HCl to remove calcite and any adhering fine grained particles.

Table 4. Purity of samples

Mineral	Purity (%)	Impurities
Stockdale Magnetite	98.0	magnetite rich silica and serpentine
Stockdale Serpentine	97.5	phlogopite, silica, and garnet
Stockdale Chromite	99.0	silica and serpentine
Stockdale Green Garnet	100.0	
Stockdale Red Garnet	100.0	
Stockdale Phlogopite	100.0	
Bala Magnetite	99.0	magnetite rich serpentine
Bala Serpentine	97.0	chromite and magnetite

The hand picked garnet and chromite fractions were purified by use of a Frantz Isodynamic Magnetic Separator in the inclined-feed position. The samples were crushed to -35 mesh and run through the Separator. The garnet fraction was further purified by crushing and sieving. The alteration products were found to be in the finest fraction, leaving coarser fractions pure. This instrument was also used to separate serpentine from the Stockdale and Bala samples. Separator settings used to achieve the separations were determined by trial and error, although suggestions from Hess (1959) and Flinter (1959) were helpful (see Table 5.). Each sample was observed under the binocular microscope and purified by hand picking if necessary and when possible.

Two varieties of garnet were separated from the Stockdale sample and were subsequently analyzed by X-ray diffraction to determine their mineralogic

Table 5. Settings for Frantz separations.

Mineral		Positive Slope (in degrees) ::Forward	Side	Current	Magnetic Fraction	Non-magnetic Fraction
Chromite	Stk*	15	15	.35	chromite	
Garnet	Stk	15	15	.35		garnet
Garnet	Stk	15	3	.00	garnet	alteration products
Garnet	Stk	10	15	.55	green garnet	red garnet
Serpentine	Stk	10	20	.85	serpentine	silica
Serpentine	Stk	30	30	.20	magnetite rich silica	serpentine
Serpentine	Stk	20	10	.40	magnetic serpentine	serpentine
Serpentine	Bala	15	30	.50	serpentine	non-magnetic products
Serpentine	Bala	20	10	.07	magnetic serpentine	serpentine
Serpentine	Bala	20	10	.18	serpentine	

Stk* - Stockdale

structure. The results appear later in this report.

Final Preparation. When the minerals were separated and purified, each sample was crushed to a very fine powder in a stainless steel mortar and pestle capsule mounted in a Wig-l-Bug vibrator. After crushing, the sample was combined with chemically pure $SrCO_3$ in the ratio of 1:1 and mixed in a previously cleaned (soap and water scrubbing, then rinsed with vycor distilled HCl, demineralized H_2O, and acetone) bakelite capsule in the Wig-l-Bug. Strontium Carbonate was added to insure a smoother arcing and Sr may, under favorable conditions, be used as an internal standard. After mixing, the sample was ready for electrode loading.

Rock standards of granite, G-1, and diabase, W-1, were obtained from the United States Geological Survey. A third standard was made by mixing equal

portions of G-1 and W-1. Each of these standards were mixed 1:1 with C. P. $SrCO_3$ as described above. The concentrations of elements in these three standards are shown in table 6 (Ahrens and Taylor, 1961).

Table 6.   Concentrations of elements in the standards.
(in parts per million, ppm)

Standard	: Cu	: Co	: Ni	: Ti	: Cr	: Zr
G-1	13	2.1	1.2	1500	22	200
G-1,W-1	60	23	42	3950	73	150
W-1	107	44	82	6400	124	100

Spectrographic Procedures

Loading Procedure.   Spectroscopically pure 3/16" diam. by 1" length graphite rods with a 1/8" diam. by 3 mm. deep crater were used as sample electrodes. Spectroscopically pure 3/16" diam. pointed carbon rods were used as counter electrodes. To prevent hand contamination, tweezers and clean weighing paper were used during the drilling, filling, and arcing. These tweezers and the loading equipment, spatula, electrode holder, and tamp were cleaned in the same manner as the Wig-1-Bug capsules. Prior to loading, the electrodes were kept in parafilm covered beakers.

The sample electrodes were loaded by taking random grab samples of the larger samples and tamping each electrode with the same amount of pressure thereby getting essentially the same amount of sample in each. A Mettler balance was employed in the earlier phases of the study to insure that each electrode received, within limits of allowable error, the same amount of sample. After each sample was loaded in duplicate, the loading instruments were thoroughly cleaned.

Arcing Procedure.   The samples were arced by a Bausch and Lomb large littrow emmission spectrograph using quartz optics. Spectrograph settings and the use of Kodak 103-O Spectrographic plates permitted a range of wavelength from 2900 A to 4800 A to be recorded. Before arcing the slit (.020 mm.) was checked and, if dirty, cleaned by use of an ultrasonic vibrator. Two graphite electrodes were then arced to insure that the source was focussed on the slit. A step sector was placed in front of the slit and five of these steps were used for the spectrum. Before the samples were arced in duplicate, the electrode holders and stand were cleaned. The electrodes were handled with tweezers. The arc was struck by touching the electrodes together then separating them. The shutter was opened as soon as the images of the electrodes were clear of the slit. An arcing current of about 7 amperes (open circuit voltage of 300v D. C.) was used because it permitted smoother arcing than a higher current. All samples were arced to completion, typically 2 minutes to 2 minutes 20 seconds. Most samples arced satisfactorily; however, phlogopite, garnet and sometimes serpentine sputtered and popped. This was solved by packing the phlogopite very tightly followed by preheating. This procedure involved placing the electrodes in contact so as to heat the sample electrode to drive off excess water, thus fusing the sample. The garnet and serpentine samples were also preheated. After each spectrum was taken, the plate was racked to a new position. Six spectra were recorded on each plate.

The plates were developed in Kodak developer for 3.5 minutes, followed by a 17 minute fix period, a 50 minute water wash, and then a 10 minute electrical drying period. As 103-O plates are optically fast, the spectra were quite dark. Another problem of slight light leakage was partially solved by taping possible leaks.

Data Processing.   Data was read from the plates by using an A.R.L.-Dietert

Table 7. Spectral lines used and their sensitivities.

Element	Wavelength (A)	Intensity	Sensitivity (ppm)
Zr	4687.8	125	40
Cr	4254.3	5000R*	50
Ti	3653.5	500	50
Co	3453.5	3000R	10
Ni	3414.8	1000R	10
Cu	3274.0	3000R	2

R* - wide self-reversal for large concentrations

densitometer. Since the spectra were dark, readings of both background and line intensity were taken. The lines used and their sensitivities are shown in table 7. From each plate, data for three calibration curves and line and background intensities were collected. In addition, data for line intensity of Fe 3450 and Sr 3464 were recorded. These two readings were taken in the hope that they could be used as internal standards. Use of an internal standard is the preferrable method of attack for such an investigation but was not used. As stated in Ahrens and Taylor (1961), there are two conditions under which the use of an internal standard is not necessary. These are (1) when a sample is arced smoothly for more than a minute, and (2) when the elemental concentration in the sample and in the standard are approximately equal. Both of these conditions were basically met in this investigation. However, this does not mean that the composition of samples and standards is the same but that elemental concentration is similar and that both, except for magnetite and chromite, have silicate matrices. In addition to this, approximately the same amount of sample was arced each time. The attempt to use Sr as an internal standard was frustrated by extreme line intensity and line interference. Iron could not be used except to narrow the range of values of a single phase.

Method.   The method used in this investigation has been described by
Ahrens and Taylor (1961). The validity of quantitative analysis from spectro-
graphic plates depends upon the assumption that the concentration of an
element in the sample is directly related to the intensity, or opacity, of
its line on the spectrographic plate. This is done in two steps involving
construction of a calibration curve and a working curve. The calibration
curve is constructed first by plotting the deflection of the densitometer
reading versus the relative intensity. The relative intensity is known be-
cause each step in the step sector is constructed so as to transmit $1\frac{1}{2}$ times
as much light as the previous step. These two readings were then plotted
on log log paper and the curve drawn. A typical calibration curve is shown
in figure 1. The upper dashed curve represents loci of points of line de-
flection versus line relative intensity. The solid curve represents the
combination of the two and is used to measure relative intensities from de-
flection data. The second step in this method involves the construction of
a working curve which relates concentration of the analysis element in the
sample to its relative intensity. This curve is obtained by analyzing a
plate of standards of known concentration, then plotting these two quantities
versus each other on log log paper. The working curve used for Ti in this
study is shown in figure 2. Working curves were constructed from the standard
plate for each of the elements studied. Deflection readings from the standard
plate were recorded twice and the working curves were obtained from a compar-
ison of both sets of data. In each case, the second curve was used because
of better analytical control. The working curves for Ti, Cu and Cr were
essentially identical, whereas Co, Ni and Zr exhibited a significant change
of slope.

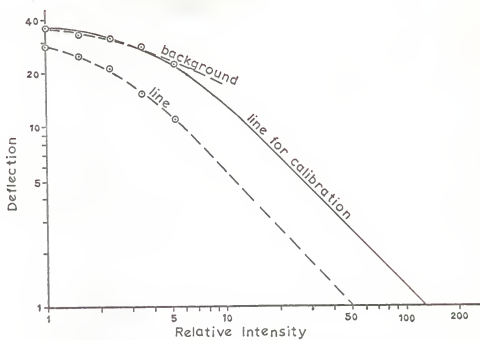One standard sample was arced in duplicate on each plate. Densitometer

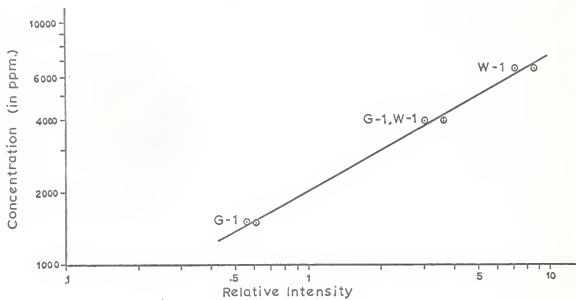Figure 1. Calibration Curve for 4690 A.

Figure 1. Working Curve for Ti.

recordings were taken from each plate and calibration curves were constructed as previously described. The position of the working curve for the particular element was found by plotting the two points of known standard concentration versus relative intensity and then drawing a line through their median point with the same slope as the working curve derived from the standard plate. The line relative intensity was found by subtracting the background relative intensity from the total line plus background reading. The concentrations of the elements in the other four spectra were then determined from the working curves using the relative intensities obtained from the calibration curves. This procedure was repeated for each line (element) on every plate.

There are three possible sources of background. These are: (1) a background of constant intensity due to extraneous light entering during arcing, (2) a variable intensity background caused by leakage, and (3) a background of variable intensity caused by emulsion irregularities. All of these causes of background errors were corrected for the analyses.

Errors. There are at least five major sources of error in this type of investigation. They are: (1) contamination, (2) erratic arcing, (3) border line sensitivity, (4) erroneous working curves, and (5) interfering lines. Of these five sources, erroneous working curves are the least likely due to the reasons discussed previously. Readings near the border line of sensitivity could be in error because it is possible that the slope of the calibration curve may change in that particular area. This source of error probably is insignificant.

Errors due to line interference are possible but unlikely. All of the lines in the immediate area of the lines inspected are of a much lower intensity and, in general, not due to common rock forming elements. Only for Ti and Ni is there any chance of interference. Ti has a possibility of inter-

ference from Cr in an extremely rich Cr phase. Ni has two chances for inter-
ference; from Co only in Co-rich sulfide minerals, and from Zr in Ni-poor,
Zr-rich phases (Ahrens and Taylor, 1961). Both of these conditions do not
apply in this case.

Erratic arcing and contamination are definite factors to be considered.
Erratic arcing causes errors due to incomplete volatilization of the material
and yields anomalously low results. Errors of this type are easily noted
during arcing and the results discarded. Contamination was guarded against
by thorough cleaning of all the loading instruments and by handling the
electrodes with tweezers. This type of error usually yields anomalously
high results and cannot be anticipated as can erratic arcing. Such data
was discarded.

INVESTIGATION OF A METHOD TO DETERMINE CONCENTRATION OF Rb AND Sr.

An investigation of a rapid method for determination of concentrations
of Rb and Sr met with failure. Standard samples obtained from Dr. Brookings
were loaded as described previously without use of an internal standard or
mixing with diluent. These samples were arced in duplicate and the data
processed in the manner previously described. Results were poor and thought
to be due to the matrix effect. To eliminate this effect, four grams of
each sample were converted to fluorides. This was done by placing the samples
in teflon dish and following the procedure below:

1. 5 ml. of demineralized water were added to moisten the sample.
2. 75 ml. of reagent HF were added.
3. The contents were evaporated to near dryness with occasional stirring.
4. Steps 2 and 3 were repeated.

These fluoride samples were loaded and arced and the data processed. The re-

sults, although somewhat better than before, were still not suitable. The poor results were thought to be due to the following effects:

1. Unresolvable interference problem of Fe 4202 in the Rb 4202 line. The method of correction outlined in Ahrens and Taylor (1961) was used but with little success.
2. Low intensity of the Rb lines caused by limited arcing time (about 40 sec.). This short arcing time was needed to limit the amount of interference of CN bands. The Sr was entirely volatilized during this period whereas Rb was not.

Although the reasons for the poor results are not understood fully, the second effect noted above probably had the most influence on the results. Working curves constructed from the data had either reverse slopes or exhibited complete random scattering.

RESULTS

Spectrochemical Data

The results of the spectrochemical analyses are listed in table 8. Asterisks in table 8 indicate circumstances which caused the elimination of this data. The exclusion of this data was primarily due to possible contamination. The extreme concentration of chromium in garnets and chromite caused gross errors in Cr determination. The average concentrations of the elements in the various phases are listed in table 9. This average is the arithmetic mean, $\overline{X}$, of the values in table 8.

The standard and relative deviations of the concentration from their average value are noted in table 10. This error analysis was used for magnetite and red garnet from the Stockdale intrusions and magnetite and serpentine from the Bala intrusion. Although insufficient data was obtained to qualify for accurate use of statistical methods, the approximate accuracy of the data is indicated in table 10. Part of this inaccuracy is due to the

Table 8.   Spectrochemical Results.

Mineral	Concentrations (in ppm)					
	Cu	Co	Ni	Ti	Cr	Zr
Stockdale						
Magnetite	22	70	300	7500	270	2550
"	28	5	430	5800	170	3200
"	**	26	190	6900	1100	2470
"	**	14	240	10100	660	2500
"	10.5	2	130	4400	140	1550
"	14.5	7	130	4500	140	1600
"	28	27	105	8200	238	*
"	13.5	14	100	7600	242	*
Red Garnet	**	77	72	4900	***	
"	9.8	125	130	4300	***	160
"	9.8	69	130	4650	***	165
"	**	69	58	3800	***	155
"	33	74	58	4500	***	140
"	13.5	84	56	5800	***	98
"	14.4	79	50	4600	***	68
Green Garnet	58	70	32	5100	***	75
"	56	74	38	5700	***	80
"	94	**	57	5800	***	89
"	107	145	20.5	3900	***	56
Phlogopite	45	170	21	4500	400	65
"	27	120	18	5400	380	110
Serpentine	10.5	15	3	2750	440	145
"	9.7	19	5.4	2300	450	162
Chromite	37	210	130	16000	***	890
"	40	155	145	21000	***	1140
"	35	112	126	11000	***	380
"	27	120	110	12500	***	220
Bala						
Magnetite	18	17	**	9000	**	1460
"	7	4	52	6200	480	1460
"	11	8.5	76	5800	220	570
"	10	7.5	49	5100	180	520
"	35	22	99	8950	530	460
"	25	5	39.5	5200	630	780
Serpentine	*	12	9	6200	880	1000
"	95	32	20	5800	880	520
"	90	20	7 ⁱ	3700	560	320
"	82	47	9	5800	770	320
"	105	50	45	6200	880	960
"	124	33	16	7600	605	1480

*possible popping
** possible contamination
*** very intense line, data not taken

Table 9. Average values

Mineral	Cu	Co	Ni	Ti	Cr	Zr
			Concentration (ppm)			
Stockdale						
Magnetite	19.4	20.6	203.1	6875	370	2312
Red Garnet	16.1	82.4	79.1	4650		131
Green Garnet	78.8	96.3	36.9	5125		75
Phlogopite	36.0	145.0	19.5	4950	390	88
Serpentine	10.0	17.0	4.2	2525	445	154
Chromite	34.8	149.2	126.2	15125		658
Bala						
Magnetite	17.7	10.7	63.1	6708	408	875
Serpentine	99.2	32.3	17.7	5883	762	767

Table 10. Standard deviation and relative
deviation of average data

	Stockdale Magnetite		Stockdale Red Garnet		Bala Magnetite		Bala Serpentine	
	s($\pm$)	C(%)	s($\pm$)	C(%)	s($\pm$)	C(%)	s($\pm$)	C(%)
Cu	7.6	39.4	9.7	60.1	10.7	60.4	16.2	16.3
Co	22.0	106.9	19.5	23.7	7.2	67.3	14.8	45.7
Ni	116.9	57.5	35.4	44.7	23.2	36.7	14.3	80.6
Ti	1540.0	22.4	553.0	11.9	1801.0.	26.8	1259.0	21.4
Cr	339.0	91.6			216.6	53.1	146.4	19.2
Zr	631.0	27.3	39.3	30.0	465.0	53.1	460.6	60.0

Standard deviation: $s = \pm \sqrt{d^2/(n-1)}$

Relative deviation: $C = \dfrac{s}{\bar{X}} \times 100$

low concentration of several of the elements measured. The method of deter-
mining the standard and relative deviations is that described in Ahren and
Taylor (1961).

Garnet Analysis

An attempt was made to calculate, from the chemical analysis (see table
2b.), the molecular percent of the garnet and members. The red garnet was
calculated to be 58% pyrope and 16% Uvarovite. More complete determination

was thwarted due to insufficient divalent elements to balance the remaining trivalent elements. The lack of FeO in the analysis is questioned since the environment in which these garnets crystallized was probably near-ultrabasic and, therefore, supposedly rich in Fe^{2+}.

X-ray diffraction analysis of the two types of garnets separated from the Stockdale sample was done to determine the dominant garnet variety present. The "d spacing", dA, and relative intensities, I/I_1, of the lines measured are listed in table 11. The Miller Indices were taken from the A.S.T.M. index card, No. 2-1008, for pyrope by comparison of dA values. Comparison of the Stockdale garnets with patterns of several garnet varieties is shown in table 12. Stockwell (1927) states that pyrope can be distinquished from other varieties by the relative intensity of the line representing the Miller Indices of 332. The relative intensities and positions of the lines are similar to the suggested values so the garnets were determined to be pyrope. Comparison of X-ray results of the two garnets suggests that the green garnet does not contain as much pyrope as the red garnet. Positive determination of the relative amounts of other garnet varieties present in the two garnets could not be made.

Table 11. X-ray results

	Red Garnet		Green Garnet	
hkl	dA	I/I_1	dA	I/I_1
400	2.889	58.4	2.891	64.6
420	2.584	100.0	2.584	100.0
332	2.464	36.4	2.466	24.9
422	2.366	32.0	2.360	38.9
510	2.267	30.2	2.270	33.1
521	2.109	36.2	2.110	24.9
440	2.032	17.8		
611	1.873	29.7	1.875	27.2
620	1.827	17.8	1.829	19.3
444	1.667	21.8	1.668	22.7
640	1.601	31.7	1.602	36.1
642	1.543	55.3	1.545	42.5
800	1.444	21.3	1.446	21.5
840-	1.291	20.8	1.292	19.3
842	1.261	31.8	1.261	21.5
921			1.247	17.0
664	1.231	17.8	1.233	19.3
941	1.167	16.8		

dA "d" spacing
I/I_1 Relative intensity

Table 12. Comparison of sample with garnet species.

	dA						
hkl	Garnet	Garnet	Almandite	Pyrope	Spessartite	Uvarovite	Grossularite
400	2.889	2.891	2.873	2.88	2.90	2.999	2.96
420	2.584	2.584	2.569	2.58	2.60	2.684	2.65
332	2.464	2.466	2.447	2.46	2.48	2.557	2.53
422	2.366	2.360	2.348	2.35	2.37	2.449	2.44
510	2.267	2.270	2.267	2.26			2.33
521	2.109	2.110	2.102	2.10	2.12	2.191	2.16
611	1.873	1.875	1.856	1.87		1.946	1.92
640	1.601	1.602	1.599	1.60	1.61	1.664	1.65
642	1.543	1.545	1.540	1.54	1.55	1.603	1.58

DISCUSSION

Elements

Copper. Copper is a strongly chalcophilic element (Goldschmidt, 1958),
but in sulfur deficient environments it is concentrated in minerals formed
during the earliest stages of crystallization (Wager and Mitchell, 1951).
Goldschmidt (1958) observed that the concentration of copper in igneous
rocks is inversely proportional to the amount of silica. Copper may occur
in valence states of +2 or +1. Ringwood (1955) states that Cu^{1+} is camou-
flaged by Na^{1+} and that Cu^{2+} is camouflaged by Fe^{2+}. Ionic radii and electro-
negativities of the elements under consideration are listed in table 13. A
possibility for diadochy of Cu^{2+} and Mg^{2+} exists but is unlikely due to the
large difference in their electronegativities. In these ultramafic rocks,
Cu is expected to be divalent and diadochic with Fe^{2+} in ferromagnesian
minerals. Although Cu^{2+} is camouflaged by Fe^{2+}, it is weakly bonded and
may thus enter ionic solutions during weathering (Rankama and Shama, 1950).

The results show that the concentrations of copper in the Bala intrusion
are slightly less than that of an average ultramafic rock and that the concen-
trations of copper in the Stockdale intrusion is much less than that of an
average ultramafic rock (see table 14). Serpentine constitutes at least 60%
of the rock, except inclusions; so is assumed to be representative of the
rock. The tacit assumption of the previous statement is that the elemental
concentrations in serpentine is similar to those of the primary olivine and
pyroxene. Serpentinization probably occurred in an environment incapable of
permitting substantial gain or loss of trace elements from the original
olivine and pyroxene. If one assumes both intrusions to have similar copper
content, the comparison of the concentration of copper in the serpentines is

Table 13.   Ionic radii and electronegativities.*

element	valence	radius	electronegativity
Al	3	.50Å	1.5
Ca	2	.99	1.0
Cr	2	.84	
	3	.63	1.6
	6	.52	
Co	2	.74	1.7
	3	.65	
Cu	1	.96	
	2	.72	2.0
Fe	2	.76	1.65
	3	.64	1.8
Mg	2	.66	1.2
Ni	2	.69	1.7
Si	4	.41	
Ti	3	.76	
	4	.68	1.6
Zr	4	.80	1.6

* after Fyfe (1964) and Ringwood (1955)

Table 14.   Concentration of trace elements in an
average ultramafic igneous rock.

element	Wager & Mitchell (1951)	Rankama & Sahama (1950)
Cr	5000 ppm	3400 g/ton
Ti	900–8000	
Ni	4000	3160
Co	300	237
Cu	150	149
Zr	30	60

interesting.   The validity of this assumption is supported by the two in-
trusions petrographic similarity and similar concentrations of Cu in the
magnetite.   The differences in copper concentrations are explained by consid-
eration of two things; (1) copper entering ionic solution easily and (2)
petrographic evidence of subsequent solution.   This difference in copper
concentration is due to subsequent solution in the Stockdale intrusion.
Copper concentration in the two magnetites are similar as is the concentra-
tion in chromite and phlogopite.   The differences in the copper concentra-
tion of the garnets may be due to prior crystallization of green garnet or
to enrichment of Fe^{2+} in green garnet.   The extent that this effect has on
chromite and phlogopite cannot be known from the existing Cu data.   Since
chromite and magnetite are structurally similar and have similar numbers of
divalent sites, Cu data suggests magnetite may have crystallized after
chromite.

    Cobalt.   Although cobalt is a chalcophilic and siderophilic element,
it is incorporated into silicate structures much more readily than copper.
The two valence states of cobalt are +2 and +3. Co^{2+} is primarily camouflaged
by Fe^{2+} although diadochy with Mg^{2+} also occurs. Co^{3+} substitutes for Fe^{3+},
but this seldom occurs (Goldschmidt, 1954).   Cobalt is enriched in early
crystallizates but does not decrease as sharply as copper or nickel with
progressive crystallization.   In some cases the concentration of cobalt is
observed to be nearly constant (Nockolds and Allen, 1954, 1956).

    The results show that the concentration of Co in these intrusions is
definitely less than that in the average ultramafic rock.   As in the case of
copper, the concentration of cobalt is shown to be lower in Stockdale serpen-
tine than in Bala serpentine.   This further supports the belief that solutions
leached some trace elements from the Stockdale serpentine.   The concentrations

of cobalt in the two magnetites are not the same, but similar. The order of crystallization of the phases in the Stockdale intrusion cannot be stated with certainty. However, Co data may indicate that magnetite and serpentine crystallized after the other phases. The sequence of crystallization of the other phases is questionable. Chromite can be considered to have crystallized first, followed by phlogopite and the garnets.

Nickel. Nickel is enriched in the earliest crystallizates. Vogt (1923) showed that (1) nickel normally occurs in magnesium silicates, (2) nickel increased with increasing magnesium content and decreased with increasing iron content, and (3) in silicates having the same Mg/Fe ratio, olivine was richest in nickel, followed by orthopyroxene, clinopyroxene, and amphibole. Rankama and Sahama (1950) and Goldschmidt (1958) also state that nickel follows magnesium. Despite the general acceptance of nickel-magnesium diadochy, Ringwood (1955) proposed that nickel actually is more likely to be camouflaged by Fe^{2+} than Mg^{2+}. His arguments were based essentially on electronegativities and ionic radii. The substitution of Ni^{2+} for $Mg^{2+}$was rejected because the higher electronegativity of the former produced a lower oxygen bond strength and the larger size of Ni^{2+} further weakened the bond. $Ni^{2+}-Fe^{2+}$diadochy was supported by their similar electronegativities and the smaller size of the Ni^{2+}ion. The apparent substitution of Ni^{2+} for Mg^{2+}observed by Vogt and others is actually due to Ni^{2+}being concentrated relative to Fe^{2+}in early phases (Ringwood, 1955). Nockolds and Allen (1954, 1956) and Wager and Mitchell (1951) have shown that the high initial concentration of nickel decreases rapidly as crystallization progresses. However, in several cases nickel concentration was observed to increase in late stage crystallizates.

The concentration of nickel in these intrusions is much lower than in

an average ultramafic rock. The results show minerals having considerable amounts of Fe^{2+} to be enriched in Ni^{2+}. Since both Stockdale chromite and Stockdale magnetite are structurally similar, the difference of nickel concentration may be due to prior magnetite crystallization or the concentration of Fe^{2+} in magnetite relative to Ni^{2+} may be camouflaged by re-enrichment of the magma in late stages, or a combination of both these effects. Higher nickel concentration in red garnet suggests that it crystallized before green garnet. However, when the error analysis is considered, the possibility of cogenesis cannot be rejected. Data of Turekian (1963) suggests that garnets are universally nickel-poor and this study supports this view. The nickel concentration data suggests an order of crystallization for the Stockdale intrusion, excluding serpentine, of: magnetite, chromite, red garnet and green garnet, and phlogopite. If late stage enrichment of Ni is considered, magnetite may have crystallized late. Comparison of the values of concentration for Bala serpentine and Stockdale serpentine again indicate solution has occurred in the Stockdale intrusion. The reason for the significant difference in concentration of nickel between the two magnetites is not clear. The most likely possibilities suggested are: (1) Bala magnetite is of secondary origin, (2) Bala magnetite is primary and represents development at a later magmatic stage than that of Stockdale, or (3) the Stockdale intrusion was enriched in nickel during late stage crystallization.

Chromium. Chromium commonly occurs in +2, +3, and +6 valence states. Cr^{3+} is the most dominant of these and exhibits diadochy with Al^{3+} and Fe^{3+} (Goldschmidt, 1958). Since Cr^{2+} mainly occurs in sulfides and Cr^{6+} as complex ions in chromates, Cr^{3+} is the only ion that needs to be considered

for this study. Ringwood (1955) states that the electronegativities of Fe^{3+} and Cr^{3+} are such that Cr^{3+} is preferred relative to Fe^{3+} in minerals and thus is enriched in early crystallizates. Turekian (1963) proposed that chromium and nickel move together in kimberlites.

Results indicate that the garnet and chromite crystallized first and that crystallization of magnetite, phlogopite, and serpentine occurred later. Comparison of the two magnetites show similar concentration of chromium. The higher concentration of chromium in Bala serpentine indicates possible contamination by chromite or represents early crystallized phases. The concentration of chromium in these intrusions is less than that in an average ultramafic rock.

Titanium. The strongly lithophilic character of titanium is reflected in its higher concentration than the previous elements. It does not form simple silicates of its own but enters into minerals as a minor element. Rankama and Sahama (1950) state that titanium is enriched in early phases of the crystallizing magma. Consideration of electronegativities prompted Ringwood (1955) to state that titanium is a complex forming ion that is concentrated in residual magmas. However, he points out that under conditions of low ionic potential titanium tends to occur as free ions in the magma. The main valence states of titanium are +3 and +4. Ti^{4+} is camouflaged by Fe^{3+} in ferromagnesian minerals. Ti^{3+} only rarely occurs in trace amounts in titaniferous pyroxene, amphibole, and biotite (Goldschmidt, 1958). There is evidence that Ti^{3+} and Fe^{3+} do not occur in the same mineral (Goldschmidt, 1958), but Rankama and Sahama (1950) contend that Ti^{3+} may substitute for Al^{3+}, Fe^{3+}, and sometimes Mg^{2+}. Consideration of ionic radii indicates a possible diadochy between Ti^{3+} and Fe^{2+}.

Results show that the titanium content of these two intrusions is similar to that of average ultramafic rocks. The concentration of Ti in the magnetite from both intrusions is essentially the same while the serpentines show a marked difference. This difference could be due to possible contamination of Bala serpentine by magnetite or chromite. The high Ti content in chromite results from early crystallization of the chromite. Phlogopite and red and green garnet have comparable Ti content. This does not mean that phlogopite and red and green garnet are cogenetic. Although they have less titanium than magnetite, phlogopite and red and green garnet can be considered to have crystallized prior to magnetite since they have less sites for possible titanium diadochy.

Buddington, Fahey, and Vlisidis (1955) have proposed a method of estimating temperatures of formation of magnetite by its content of TiO_2. They found that the bulk composition of a rock has little influence on the temperature determination. Conditions for the application of titanium thermometry are that iron-titanium oxides are essentially ilmenite and titaniferous magnetite, and that titanium content in these minerals is a direct function of temperature alone. In his reply to Heier (1956), Buddington (1956) states that the effect of pressure at a depth of 10 km. is offset by the presence of 1% additional water. The application of this method of temperature determination to the Bala and Stockdale intrusions is justified because the above mentioned conditions are essentially met. Petrographic study indicates that both ilmenite and titaniferous magnetite occur in these intrusions. The pressure involved in serpentinization and injection is no higher than the pressure to which Buddington alluded (Bowen and Tuttle, 1949). The presence of water to offset pressure effects is assured by the very nature of ser-

pentinization thus permitting temperature to be the dominant factor govern-
ing Ti distribution. The concentration of TiO_2 in Bala magnetite and
Stockdale magnetite is 1.11% and 1.14% respectively. These concentrations
correspond to a temperature range of 400°C to 550°C.

   Zirconium. Ringwood (1955) classed zirconium with titanium in that they
form complex ions and are usually enriched in late crystallizates. Zirconium,
like titanium, is also capable of occurring in the magma as free ions. Unlike
titanium, zirconium forms simple silicates (i.e. zircon). Zirconium is en-
riched in late stage minerals; and although the ionic radius of Zr^{4+} is large,
its coordination number can be six (Rankama and Sahama, 1950). Considering
the ionic radius and electronegativity of Zr^{4+}, substitution for Ti^{4+} or Fe^{2+}
seems possible. From previous trace element studies, Brookins and Dennen
(1964) have proposed that diadochy between Zr^{4+} and Ti^{4+} is more common than
previously thought.

   The results show that the intrusions are enriched in zirconium compared
to the average ultramafic rock (see Table 14.). Phlogopite, green and red
garnet, and Stockdale serpentine have low concentrations of zirconium indi-
cating early crystallization and lack of sites favorable to Zr^{4+}. The high
concentrations of zirconium in chromite and especially in magnetite are
possibly due to late crystallization and availability of ions capable of
diadochy. The similar concentration of zirconium in Bala magnetite and Bala
serpentine suggest they are cogenetic or possible contamination of Bala
serpentine with magnetite or chromite has occurred (see Table 4.). Comparison
of the two serpentines supports the latter of these suggestions. The dif-
ference in the two magnetites is attributed to either a difference in stage
of crystallization or possible difference in concentration of zirconium in

Table 15. Ratios of concentrations.

Mineral	Co/Ni	Cr/Ni	Co/Ti	Cu/Ti	Zr/Ti	Co/Zr
Stockdale						
Magnetite	.101	1.82	.00300	.00282	.3363	.0090
Red Garnet	1.042		.01772	.00346	.0282	.6290
Green Garnet	2.610		.01879	.01537	.0146	1.2840
Serpentine	4.048	105.95	.00673	.00396	.0610	.1104
Phlogopite	7.436	20.00	.02929	.00727	.0178	1.6477
Chromite	1.182		.00986	.00230	.0435	.2268
Bala						
Magnetite	.170	6.47	.00160	.00264	.1304	.0122
Serpentine	1.825	43.05	.00549	.01686	.1304	.4211

the original magma.

Concentration Ratios

Concentration ratios between various elements are listed in table 15. These ratios were picked to show if definite trends appear in the results. Elemental diadochy is evidenced by a constant ratio. Variance of the ratio indicates that one element may substitute into a second position in that phase or that post-crystallization effects have added or removed elements from the phase.

Zr/Ti. This ratio was chosen to determine the possibility of diadochy between titanium and zirconium. The value of the ratio of Zr/Ti is indicated in table 15. The constant value of Zr/Ti for Bala serpentine and magnetite indicates near contemporaneous crystallization. Zr/Ti is essentially constant for red and green garnet, phlogopite, and chromite thus indicating that Ti-Zr diadochy possibly existed. The small value of these ratios for phlogopite, chromite, and red and green garnet is probably due to the inability of these

structures to incorporate Zr^{4+} while Ti^{4+} can enter. The high values represent phases which crystallized late or are rich in Fe^{2+} and thus have a possibility of diadochy with Zr^{4+}.

Co/Ni. The ratio of Co/Ni is chosen because it permits an estimation of the amount of differentiation that has occurred. As seen from table 15, this ratio varies considerably. Only the ratios for the magnetites are close to the values proposed by Rankama and Sahama (1950) and Goldschmidt (1958). The remainder of the ratios show an excess of cobalt. Turekian (1963) found marked discrimination against nickel in garnets in the various samples he analyzed, and the concentration of nickel in garnet is similar to that found in this study. The lack of nickel causes the high ratios in the garnets. Phlogopite is also Ni-deficient possibly due to lack of Fe^{2+} or because it crystallized in a nickel-poor environment. Serpentine ratios reflect little in the case of Stockdale because of suggested solution effects, and may reflect previous concentrations of cobalt and nickel in the olivine and pyroxene in the Bala intrusion. The Co/Ni ratio in chromite is also high because chromite was one of the first phases to crystallize, and this indicates that the initial ratio of the magma was higher than normally expected for ultramafic magmas. The possibility of Co^{3+} being present cannot be ignored. In such a case cobalt could then compete for either +2 or +3 sites and could cause high values of the ratio.

Co/Ti. This ratio was picked to test the Co/Ni ratio. The ratios vary greatly; red and green garnet, magnetite, and the serpentine ratios are similar. Possible presence of Ti^{3+} is indicated by the chromite ratio since it is lower than normal. The ratios indicate enrichment of cobalt in the phlogopite and the garnets.

Cr/Ni. Although Turekian (1963) has shown that chromium and nickel move together, the ratios do not reflect this effect. This is expected since Ni^{2+}-Cr^{3+} diadochy is unlikely due to differing ionic radii, electronegativities, and valences.

Cu/Ti. This ratio was chosen to compare the behavior of a strongly chalcophilic element and a strongly lithophilic element. The value of this ratio are remarkably constant with the exception of green garnet, phlogopite and Bala serpentine. This indicates that copper, in the absence of sulfur, may act as a lithophilic element. It does not suggest, however, that perhaps copper tends to follow titanium, but rather that they both may be diadochic with a common element.

Co/Zr. This ratio was chosen to compare possible diadochy with a common element, Fe^{2+}. The random distribution of these values indicate that diadochy with Zr^{4+} and Fe^{2+} is not important.

CONCLUSIONS

The conclusions drawn from this study support many of the theories which pertain to serpentinization of ultramafic intrusions. The Bala and Stockdale intrusions represent rocks that have experienced some sort of differentiation prior to or concurrent with the time of injection of the magma. High Zr content, low Co and Ni concentrations, and high Co/Ni ratios support the conclusion that these intrusions are differentiated with respect to a parent magma. Secondly, they are differentiated with respect to each other. This conclusion is supported by significant differences in zirconium and nickel content and mineralogic differences demonstrated by petrographic

studies. The type of differentiation which occurred cannot be rigidly defined due to the post-crystallization alterations.

Serpentinization occurred during injection in an essentially closed system. Had the environment been open to repeated attacks of water, elements such as copper would have been removed from the system leaving low concentrations. The concentrations of copper, cobalt, and nickel in Bala serpentine are such that when differentiation from a parent magma is considered; injection in an open system is rejected. This means that extraneous water was involved but that its involvement was limited to OH^- positions in serpentine. Although the concentrations of copper, cobalt, and nickel in Stockdale serpentine are low, it must be remembered that there is strong petrographic evidence for solution effects which could leach these elements from the serpentine. It is therefore concluded that post-emplacement solution caused the lower concentration of copper in the Stockdale intrusion.. There are many inclusions which have been serpentinized, however due to low temperature of injection and the nature of serpentinization, diffusion of the trace elements from these inclusions is expected to be very limited. Thus susceptibility of the system to contamination from inclusions is of minor importance. A completely serpentinized groundmass supports the conclusion that serpentinization occurred during injection. Had serpentinization occurred after emplacement of the magma, complete serpentinization would not be expected. In addition, post-emplacement alteration would alter the inclusions as thoroughly as the groundmass, but is not observed.

The temperature of injection for these intrusions was determined by the TiO_2 content of magnetite to be between $400°C$ and $550°C$. This is the

temperature near intrusion because the magnetite has been shown to have crystallized before most of the groundmass under near-magmatic conditions. This temperature agrees very favorably with the work on serpentinization by Bowen and Tuttle (1949).

The sequence of crystallization of the phases in the Stockdale intrusion is as follows: chromite, green garnet, red garnet, phlogopite, magnetite, and serpentine. This is not a strict sequence of crystallization since some of the phases may crystallize simultaneously or exhibit a range of crystallization. Evidence for first crystallization of chromite is based on petrographic evidence and the consistantly high concentration of copper, cobalt, nickel, titanium, and chromium. The proper sequence of crystallization of green garnet, red garnet, and phlogopite cannot be stated with certainty because nickel, cobalt, and copper concentrations each indicate different orders of crystallization of these three phases. It can be concluded that green and red garnet crystallized before phlogopite since garnets are considered high temperature minerals.

The elemental variations are consistent with geochemical theory. Copper, cobalt, titanium, and chromium are enriched in early formed crystals and decrease during crystallization, wheras zirconium shows typical enrichment in later phases. Nickel distribution is not normal in the Stockdale intrusion as enrichment occurs in early phases and late stage magnetite. This is probably due to diadochy with Fe^{2+} ans described by Ringwood (1955) or to late stage enrichment as described by Nockolds and Allen (1954,1956) and Wager and Mithcnell (1951). This latter possibility is likely because little nickel was incorporated in the garnet and phlogopite during crystallization, which is consistent with the work of Turekian (1963). It is

impossible to tell which of these effects is more important. Nickel distribution in the Bala intrusion is not similar. As garnets are not present, the magma probably was not enriched in nickel during late stage crystallization but behave normally (Wager and Mitchell, 1951 and Nockolds and Allen, 1954, 1956). Lower concentration of nickel in Bala magnetite than in Stockdale magnetite supports this conclusion. This also lends support to the conclusion that the Stockdale and Bala intrusions are differentiated with respect to each other. Diadochy between zirconium and titanium is not rigorously demonstrated but is supported by the constancy of the Zr/Ti ratios. The proposed covariance of chromium and nickel is not supported. Copper and titanium were shown to exhibit diadochy with a common element, probably Fe^{2+}.

X-ray analysis of the two varieties of garnet indicates that they are both pyrope, supporting the work of Bagrowski (1941). It was not possible to determine the amount of garnet end members in these garnet, but the red garnet is purer than the green garnet. This is supported from X-ray data by a less intense 332 peak and from trace element data by the incorporation of elements diadochic with Fe^{2+}.

From this study, little can be stated in regard to the relationships between these intrusions and the surrounding area. Since the intrusions are ultramafic, the magma must have come from a depth in the order of 35 miles. They also came through igneous and metamorphic terrains as indicated from the petrographic studies of the igneous and metamorphic inclusions by Bridge (1953). Alinement of inclusions near the country rock contacts indicates injection occurred in a molten or plastic state. Injection was controlled by lines of weakness developed in the intruded sedimentary rocks.

These lines of weakness are attributed to joint systems (Byrne, Parish, and Crumpton, 1956) or to gash fractures produced by strike slip movement in the basement complex (Taylor, 1950).

Suggested further work should include studies of K-Ar or Rb-Sr age determinations; petrography; individual phase analysis; and diffusion studies to determine temperature, distribution coefficients, and behavior of other elements.

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SPECTROCHEMICAL INVESTIGATION OF THE
BALA AND STOCKDALE INTRUSIONS,
RILEY COUNTY, KANSAS

by

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ABSTRACT

This study was an investigation of the Bala and Stockdale intrusions by emission spectrography. Chromite, two varieties of garnet, phlogopite, magnetite, and serpentine from the two serpentinized peridotite intrusions were obtained by magnetic, heavy liquid, and handpicking separations. The pure mineral separates were crushed and mixed 1:1 with C. P. SrCO₃ prior to arcing with the emission spectrograph. Samples were arced in duplicate and to completion. Rock standards, G-1, G-1:W-1::1:1, and W-1 were arced in duplicate to obtain working curves for the elements investigated, and one of these standards was arced in duplicate on each plate. An internal standard was not used. The concentrations of nickel, cobalt, copper, chromium, titanium, and zirconium in the various phases were determined.

Careful examination of these rocks in thin section permitted investigation of their mineralogy and petrology. Chromite, garnet, and phlogopite were determined to be primary phases and magnetite was shown to have crystallized under near-magmatic conditions near the time of serpentinization. Serpentine and calcite constitute about 70% to 80% of the rocks.

An attempt was made to develop a spectrographic method for the quick determination of Rb and Sr concentrations in the samples, but this was unsuccessful because of line interference, cyanogen bands, and the matrix effect.

The two varieties of garnet separated from the Stockdale intrusion were analyzed by X-ray diffraction and identified as pyrope. The red garnet is purer than the green garnet.

The TiO_2 content, 1.11% and 1.14%, of magnetite provides a method of estimating the temperature of injection of the intrusions. The resultant temperature of 400°C to 550°C compares favorable with other serpentiniza-

tion studies. Depletion of copper in the Stockdale intrusion indicates that solution has occurred, and this was supported by petrographic evidence. The sequence of crystallization was determined to be chromite, green garnet, red garnet, phlogopite, magnetite, and serpentine, although several of the ranges of crystallization certainly overlap. The relative concentrations of nickel in the phases from the Bala intrusion indicate enrichment in early crystallizates, but nickel exhibits late stage re-enrichment in the Stockdale intrusion which is probably due to the presence of garnet. Proposed diadochy between titanium and zirconium is supported but not rigorously demonstrated.

Differentiation of the intrusive magma from a parent magma is indicated by the trace element data. The mineralogic and trace element data shows that the Stockdale and Bala intrusions were differentiated relative to each other. The injection of these intrusions in an essentially closed system is supported by trace element data, low injection temperature, and serpentinization requirements.